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# FY08 Chemical Synthesis for the Self-Decontaminating Coatings Project

**by André A. Williams, Joshua A. Orlicki, Adam M. Rawlett, Wendy Kosik Chaney, and Eugene Napadensky**

**ARL-TR-6558** **August 2013**

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**14. ABSTRACT**
Pathogenic bacteria, once deposited on surfaces, can contaminate military personnel, vehicles, and other assets. This project aims to develop materials that can be integrated into current paint formulations that decontaminate surfaces to prevent bacterial infections. These materials upon integration into paint formulations will spontaneously segregate to surfaces and provide self-decontaminating surfaces. These synthesized materials consist of Boltorn hyperbranched polymers that are functionalized with hydantoin, alkyl, and perfluorinated groups.

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# 1. Introduction

The self-decontaminating coatings project is a collaborate ve effort between the U.S. Air Force Research Laboratory (AFRL), the U.S. Army Research Laboratory (ARL), the Naval Research Laboratory (NRL), and the Edgewood Chemical and Biological Center. The program focuses on the research and development of coatings with self-decontaminating or self-cleaning properties toward chemical warfare agents, such as O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX) or bis(2-chloroethyl) sulfide (HD).

Army vehicles and support equipment currently employ chemical agent resistant coatings (CARC) to minimize adsorption of chemical warfare agents (CWAs) in the event of battlefield exposure (Army Regulation 750-1). The current technology provides passive protection but has no inherent self-decontaminating capability. Materials that undergo autonomous decontamination or provide for self-cleaning characteristics could reduce the logistical footprint associated with decontamination operations and represent a significant advance for the Department of Defense (DOD). A series of additives have been evaluated for incorporation into military topcoats to improve performance against high-challenge levels (e.g., 1 $\mu g/mm^2$) of chemical warfare agents. If successful, a repellent coating is envisioned that completely prevents sorption of chemical agents, enables autonomous decontamination, reduces the volume of cleaning solution necessary to recover an asset, and enables the realization of a huge logistical and tactical benefit to the DOD.

Work at ARL consisted of extensive synthesis and analysis of various additives, as well as the formulation of those additives into surrogate test coatings for evaluation. Additives were analyzed via proton ($^1H$) and carbon ($^{13}C$) nuclear magnetic resonance (NMR). Formulation and deposition of test coatings was also performed, and surface properties were probed using x-ray photoelectron spectroscopy (XPS), accelerated weathering, and color and gloss analysis.

Efforts at AFRL initially consisted of continuing attempts to modify metal and ceramic oxides for incorporation into CARC. Modifications included both repellent and reactive moieties, as well as neat additives that provide the same functionality.

NRL studied potential additives that could be incorporated into the coatings to facilitate self-decontamination and reduce the burden on repellency.

This report is centered on work performed at ARL during FY08 in the area of synthesis and characterization of novel CWA-resistant additives developed for polyurethane topcoats based on Boltorn* H20 polymer.

* Boltorn is a registered trademark of Perstorp.

## 2. Synthesis of Hydantoin-Boltorn H20 Targets

Boltron H20 is a dendritic polymer with a highly branched polyester structure that contains theoretically 16 primary hydroxyl groups and has a molecular weight of 1747 grams per mole (g/mol), assuming an idealized structure. The high quantity of hydroxyl groups provides the opportunity for fractional modification of the chain ends and the addition of many different moieties. This approach allows the tailoring of chemical properties for specific applications. One consideration when discussing the modification of the Boltorn family of materials is that the base monomer, 2,2-bis(hydroxymethyl) propionic acid (figure 1), is an $AB_2$-type monomer. This means that each monomer contains one A group (the acid) and two B groups (alcohol), and during polymerization the A group can only react with the B group and vice versa. Because of the inherent stoichiometry of the $AB_2$ monomer the number of chain ends available for modification (n+1 and barring cyclization events) scales with the degree of polymerization (n), so that the quantity of free alcohol available for coupling in the unmodified polymer can be estimated by assuming one reactive site per monomer repeat unit equivalent weight (116.1 g/mol).

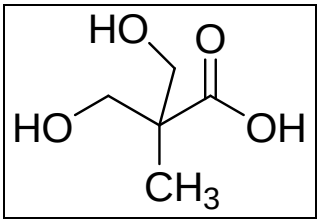


Figure 1. Structure of 2,2-bis(hydroxymethyl) propionic acid.

During this reporting period, scientists at ARL attempted to synthesize three different Boltorn H20-based molecules containing hydantoin moieties (see figure 2). In each of the three targets, hydroxyl chain ends were modified with perfluorinated octanoic acid (PFOA), lauric acid, and a hydantoin moiety.

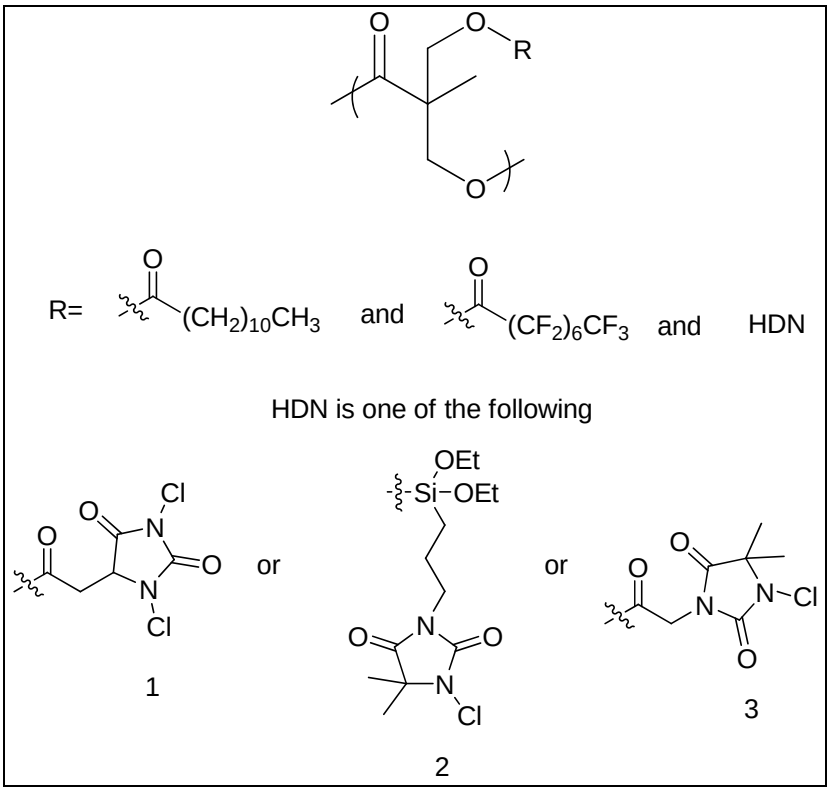


Figure 2. Synthetic targets 1–3.

Chlorinated hydantoin entities, such as *N*-chlorohydantoin, have the ability to stabilize and then release oxidative chlorine ($Cl^+$) (*1*) that enables *N*-chlorohydantoins to be used as antimicrobial agents active against both Gram (+) and Gram (-) bacteria (*1*−*8*). The retention and release of $Cl^+$ allows *N*-chloramides to act as a stabilized organic oxidizer (bleach equivalent) that can be integrated into polymers and textiles (*2*).

Researchers have also demonstrated the ability of *N*-chloramides to decontaminate chemical agent simulants (*9, 10*), which are also acting as a source of $Cl^+$. *N*-Chloramides decomposed simulants of mustard (HD and simulant 2-chloroethyl ethyl sulfide), VX, (simulant Demeton-S) (*9*), and oxidized the common thiophosphate of various organophosphate pesticides (*10*).

In almost all instances, the *N*-chlorohydantoin or *N*-chloramide can be regenerated by exposing the protonated hydantoin or amide to aqueous bleach, providing a convenient route to regenerate the reactive species. The antimicrobial activity, coupled with potential activity against chemical agents, makes *N*-chlorohydantoins attractive candidates for use in reactive coatings for autonomous surface decontamination.

## 3. Target 1 Synthesis

A one-step method to synthesize the precursor to target 1 was envisioned, where intermediate 4 was prepared by functionalizing Boltorn H20 with lauric acid, PFOA, and 5-hydantoin acetic acid via dicyclohexylcarbodiimide (DCC) coupling (figure 3). This reaction used 4-(dimethylamino) pyridinium 4-toluenesolfonate (DPTS) as a catalyst, which was reported to promote the room-temperature (rt) esterification of deactivated alcohols (phenols) (*11*). The reaction was performed in tetrahydrofuran (THF) for 14 days (d) at 60–70 °C.

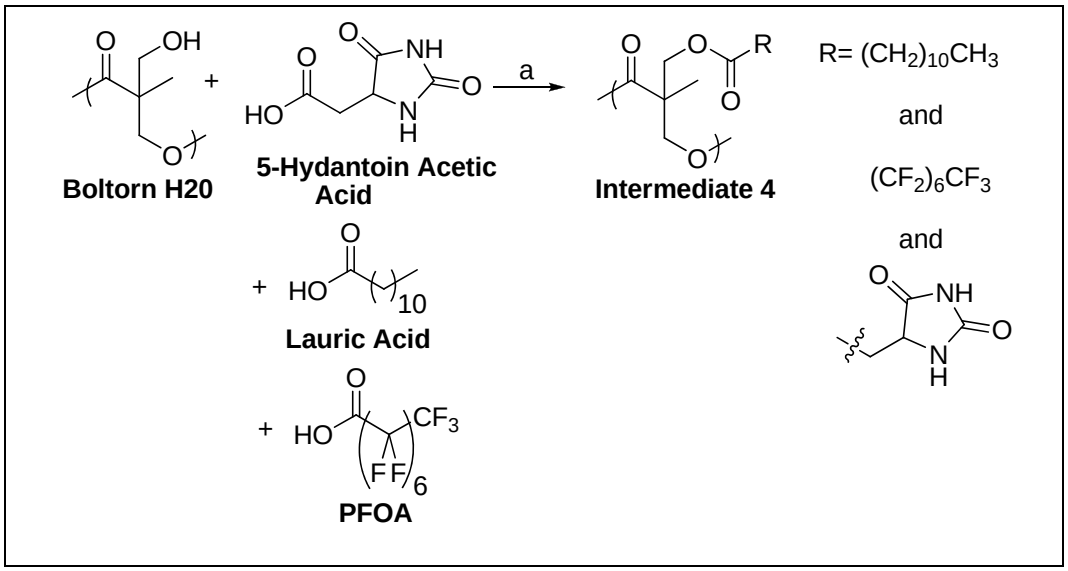


Figure 3. Coupling of 5-hydantoin acetic acid, lauric acid, and PFOA to Boltorn H20 polymer. Conditions a: DCC, DPTS, solvent, 60–70 °C, 2–14 d.

Initial reactions in THF failed. There was minimal to no attachment of the hydantoin moiety to the polymer. The lack of attachment was due to the insolubility of the Boltorn polymer in THF, even at elevated temperatures. In this instance, the increased solubility of the product relative to the starting materials was insufficient to drive the reaction toward product formation.

To overcome the insolubility of the unmodified Boltorn H20 in THF, three additional solvents were evaluated as alternatives, including pyridine, dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP). Reactions in NMP and DMF were both homogeneous and conducted at rt, whereas reactions in pyridine were maintained at 60–65 °C to improve solubility of the base Boltorn polymer. The success of a reaction was judged based on the extent of conversion of the alcohol groups of Boltorn H20 into ester groups as determined using $^{1}$H NMR spectroscopy.

### 3.1 Characterization of Targets 1–3

Samples were dissolved in either *d*-chloroform ($CDCl_3$) or *d*-dimethylsulfoxide (DMSO), and NMR ($^1H$ and $^{13}C$) spectra were obtained using a Bruker 600 MHz instrument. $^1H$ NMR was used extensively to evaluate the effects of solvents, coupling catalysts, and coupling agents on the effectiveness of attaching the hydantoin group to the base Boltorn H20 polymer. Consider first the $^1H$ NMR spectrum of unmodified Boltorn H20 shown in figure 4. The methylene groups ($-CH_2-$) of the polymer backbone could be differentiated based on whether the oxygen on the group was part of a free alcohol (-OH) or part of an ester linkage (-OCOR). The methylene group adjacent to a free alcohol was identified as peak A in figure 4 (3.48 ppm), which was shifted upfield to peak B when the oxygen was part of an ester linkage (4.13 ppm). The initial integral of the free alcohol groups was 2.08, whereas the starting integral for the ester groups was 1.00, providing for an approximate 2:1 ratio of free hydroxyl groups to esterified linear or dendritic chain segments. The success of a reaction was based on the conversion of the alcohol groups of Boltorn H20 into ester groups. As PFOA, lauric acid, or hydantoin reacted with the alcohol groups on Boltorn, the alcohol groups (peak A) were converted to ester groups (peak B). This conversion altered the original 1:2.08 ratio of esters to alcohols and can be easily monitored by NMR. Another indicator of a successful reaction was the emergence of methylene protons adjacent to the hydantoin moiety in 5-hydantoin acetic acid. When attached to the polymer these protons appeared as a singlet at 2.73 ppm.

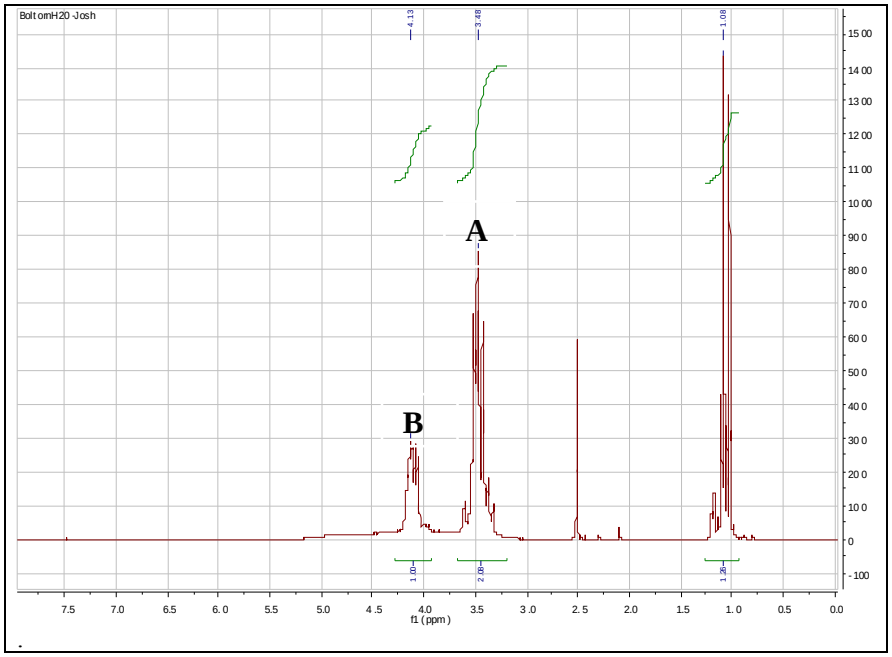


Figure 4. $^1H$ NMR spectrum of Boltorn H20. Spectrum obtained in DMSO.

### 3.2 Target 1 Reaction Optimization

In addition to changes in solvents, other reaction conditions were altered to optimize the attachment of the hydantoin group to the Boltorn H20 polymer. Other coupling catalysts, such as *N*-hydroxybenzotriazole (HOBT) and *N*,*N*-dimethylaminopyridine (DMAP), were investigated to determine whether these catalysts would increase reactivity relative to DPTS. Additionally, diisopropylcarbodiimide (DIC) was substituted for DCC to determine whether the diisopropyl urea byproduct provided for easier isolation of product, or if overall yield of the hydantoin modified polymer increased.

Alternative pathways were also devised for the synthesis of target 1. An alternate two-step synthetic scheme (figure 5) using a modified Boltorn H20 polymer (intermediate 5) was investigated. Intermediate 5 had previously been functionalized with lauryl and perfluorinated ester groups and exhibited improved solubility in a range of organic solvents. The increased solubility was sufficiently beneficial to justify the additional synthetic step.

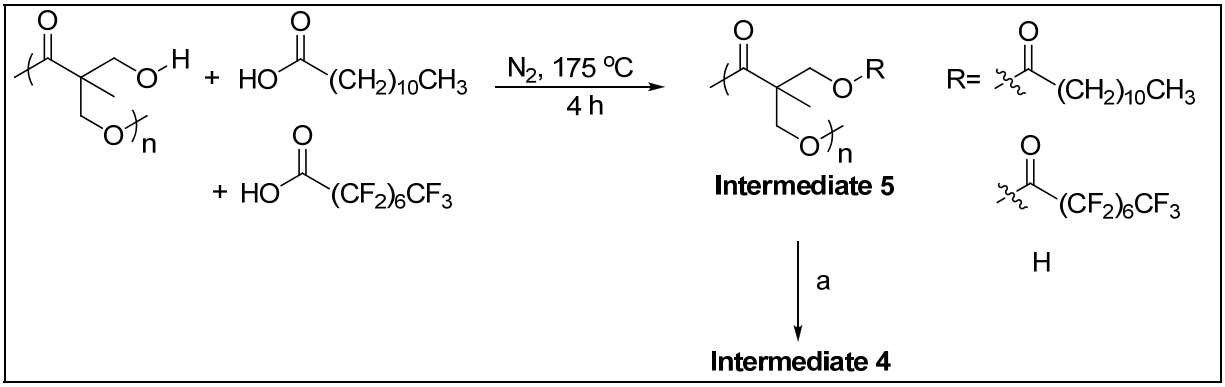


Figure 5. Synthesis of intermediate 4 via a two-step synthesis. Conditions a = DCC, HOBT, pyridine, 60 °C, 7 d.

### 3.3 Effects of Solvent on Reactivity

Initial coupling reactions in THF (figure 3) did not lead to attachment of lauric acid, PFOA, and 5-hydantoin acetic acid to Boltorn H20 polymer, presumably due to poor solubility of the base polymer in THF. Subsequent coupling reactions were performed in pyridine, NMP, and DMF to overcome the poor solubility of the unmodified polymer.

Boltorn modification in these three solvents was attempted using DCC as the coupling reagent and DMAP as the coupling catalyst. Compared to the $^{1}$H NMR spectrum of the core Boltorn polymer starting material (figure 4) all three reactions were successful. Reactions performed in each solvent led to large conversions of alcohol groups (figure 4, peak A) into ester groups (figure 4, peak B). The reactions in pyridine had an ester-group integral of 1.00 compared to an integral of 0.53 for the alcohol groups (figure 6); from NMP solvent the reaction product had an

ester-alcohol integral ratio of 1 to 0.58 (figure 7); from DMF the product exhibited an ester-alcohol ratio of 1 to 0.56 (figure 8). When compared to the starting material, which had an ester-alcohol integral ratio of 1.00 to 2.08 (figure 4), all the solvents (pyridine, NMP, and DMF) showed significantly greater conversion when compared to THF, which did not result in the desired product. The differences between pyridine, NMP, and DMF regarding extent of conversion were comparable with pyridine being marginally better than DMF and NMP. As a further confirmation of product formation the methylene protons adjacent to the hydantoin groups were present in products from reactions using NMP and pyridine (figures 6 and 5, peak C) but was obscured in the DMF reaction product due to overlap with residual solvent peaks (figure 8, peak 1).

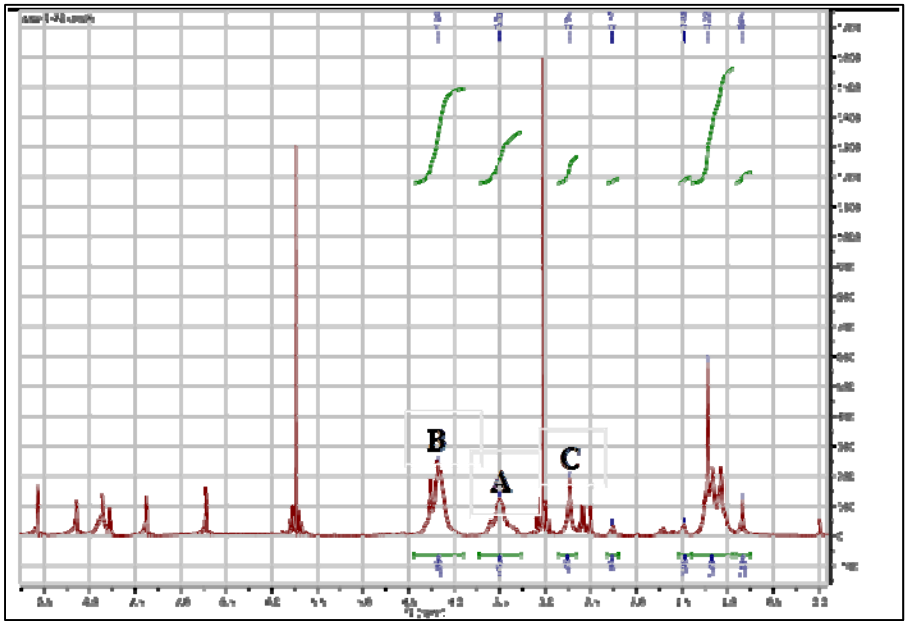


Figure 6. $^{1}$H NMR spectrum of DCC coupling reaction in pyridine.

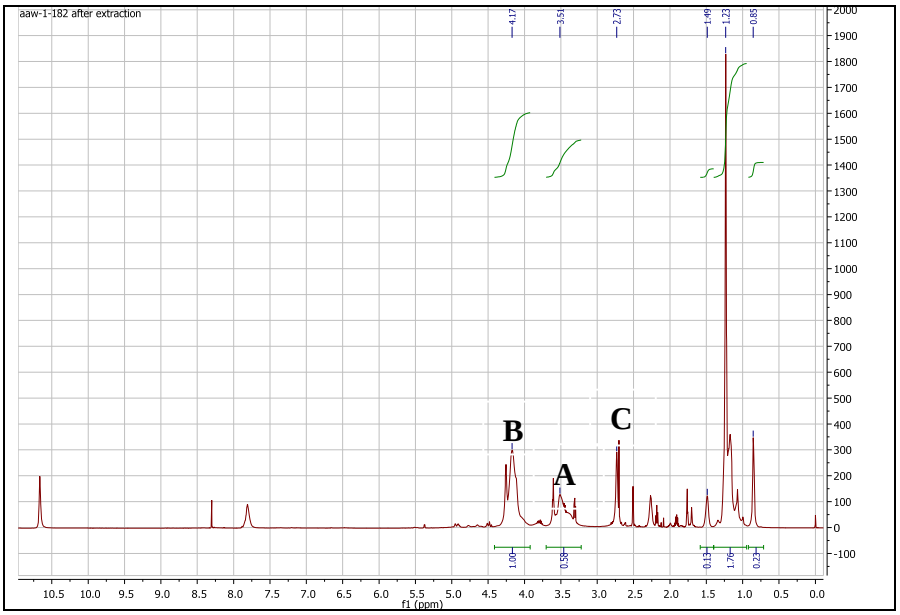


Figure 7. $^{1}$H NMR spectrum of DCC coupling reaction in NMP.

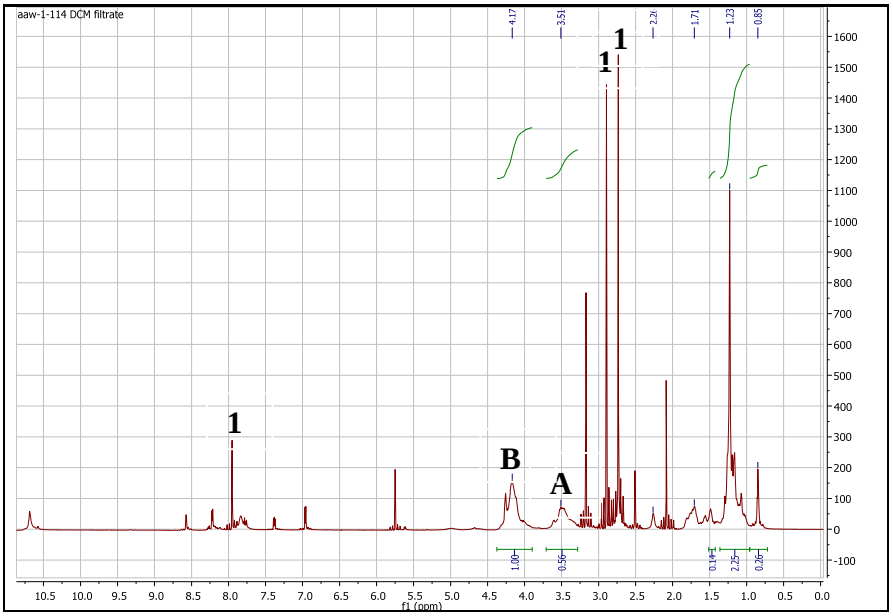


Figure 8. $^{1}$H NMR spectrum of DCC coupling reaction in DMF.

## 3.4 Effects of Coupling Catalyst on Reactivity

In another attempt to improve reactivity the effects of various coupling catalysts used to attach 5-hydantoin acetic acid to the Boltorn H20 polymer were investigated. In this study, DPTS (original catalyst), DMAP, and HOBT were compared. As noted previously, the effectiveness of the reaction was determined by measuring the conversion of the alcohol groups in the starting

material (figure 4, peak A) to ester groups (figure 4, peak B). Similar to the solvent investigation, all coupling catalysts performed similarly with respect to end group conversion. The product obtained from the reaction that used DPTS had an ester-group integral of 1.00 compared to an integral of 0.64 for the alcohol groups (figure 9). The product obtained from the reaction that used DMAP had an ester-group integral of 1.00 compared to an integral of 0.54 for the alcohol groups (figure 10). The product obtained from the reaction that used HOBT had an ester-group integral of 1.00 compared to an integral of 0.60 for the alcohol groups (figure 11). All three catalysts proved to be adequate.

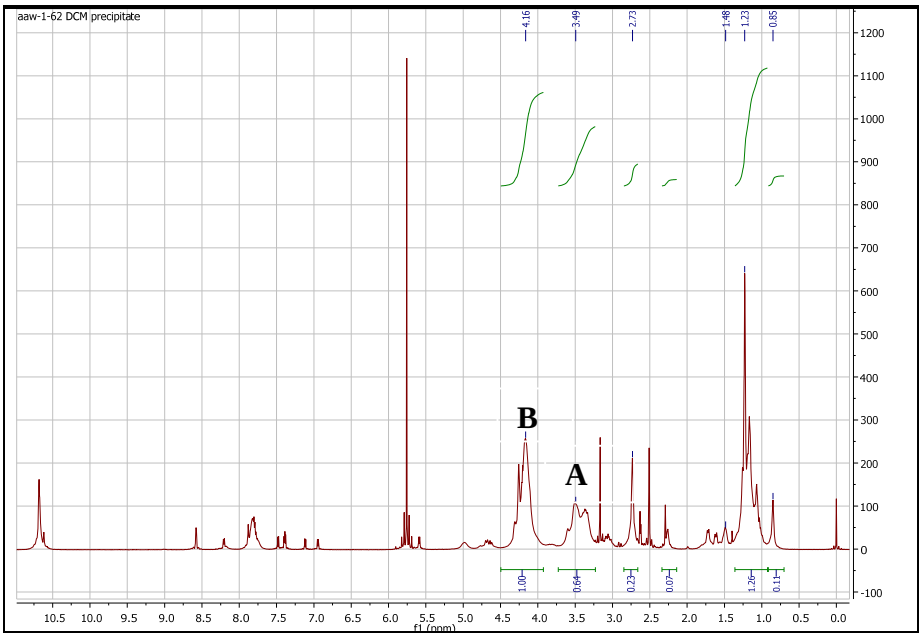


Figure 9. $^{1}$H NMR spectrum of DCC coupling using DPTS.

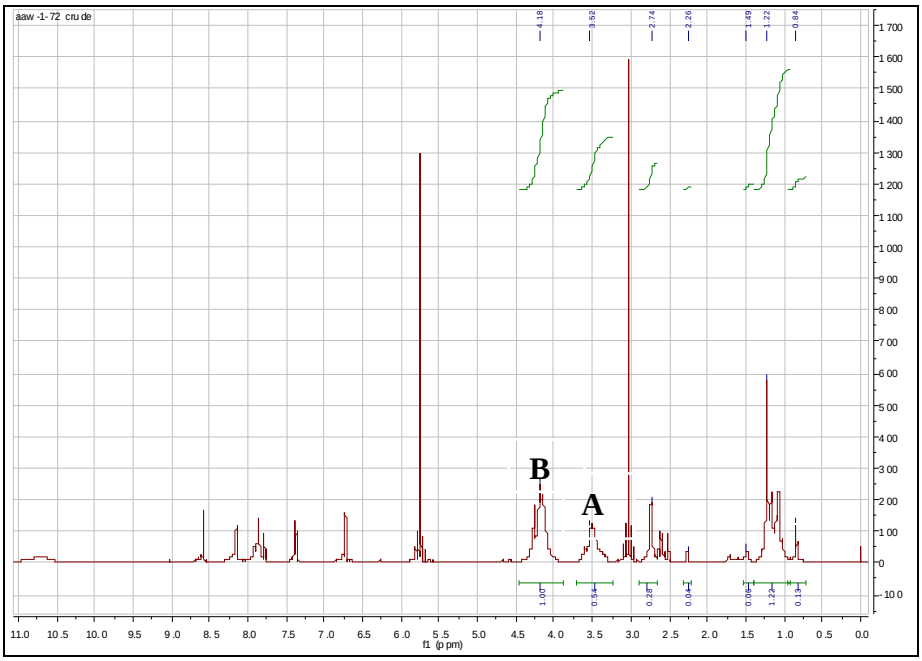


Figure 10. $^{1}$H NMR spectrum of DCC coupling using DMAP.

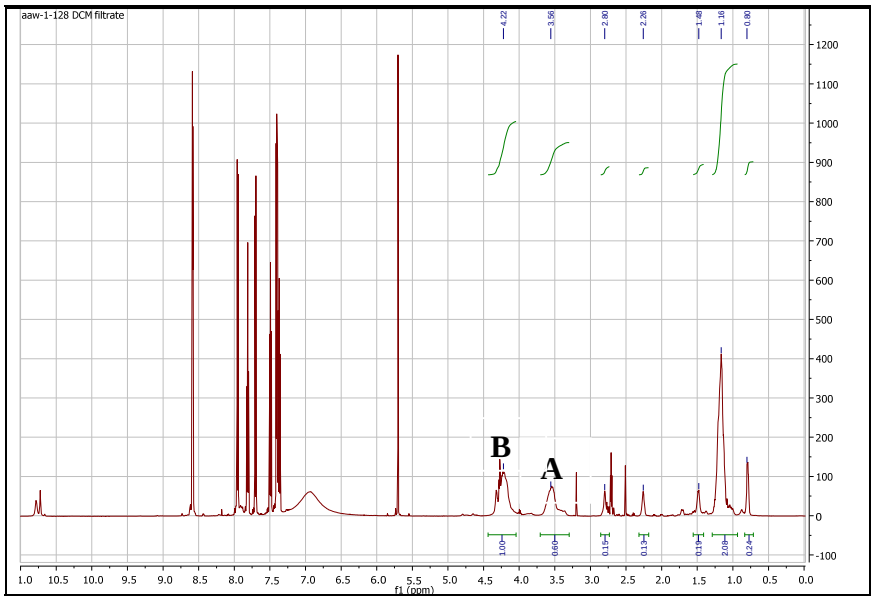


Figure 11. $^{1}$H NMR spectrum of DCC coupling using HOBT.

### 3.5 Effects of Coupling Agent on Reactivity

In addition to changes of reaction solvent and coupling catalyst, the carbodiimide coupling partner DCC was replaced with DIC to determine whether a different coupling agent would improve reactivity. During the activated ester coupling DCC was converted to dicyclohexyl urea in a direct stoichiometric ratio with the reacted alcohol and acid. The test reactions employed DMAP or HOBT as the catalyst and DMF or pyridine as the solvent. Neither reaction, in

pyridine or DMF that used DIC, yielded the desired product; therefore, the use of DIC as the coupling agent was abandoned.

### 3.6 Synthesis of Target 1 via Intermediate 5

In an alternate synthetic method en route to target 1, a modified Boltorn H20 polymer (intermediate 5) was synthesized that already contained the perfluorinated and aliphatic components. Unlike the core Boltorn H20 polymer, this intermediate was soluble in typical solvents, such as dichloromethane (DCM), THF, acetone, etc. This modified polymer was used in a coupling reaction with HOBT, DCC, and pyridine, and the reaction was conducted at 60 °C.

The reaction was successful. The initial integral of the methylene groups adjacent to the free alcohol groups (figure 12, peak A) for intermediate 5 was 0.77, whereas the starting integral for the ester group (figure 12, peak B) was 1.00. For the reaction product, the ester-alcohol integral ratio was 1 to 0.43 (figure 13), which corresponds to a 44% reduction of alcohol groups. A direct comparison cannot be made comparing the synthesis of intermediate 4 via the one-step method (figure 3) and the two-step method (figure 5) that used intermediate 5. In the DCC method, the starting ester-alcohol ratio was 1:2.03, and the best conversion led to a 1:0.54 ester-alcohol ratio. The 73% reduction of alcohol groups for the one-step method is much higher than the 44% reduction for the two-step method; however, the one-step method involved the attachment of three groups (lauryl, PFOA, and hydantoin), whereas the reaction with intermediate 5 only involved the attachment of the hydantoin group. Although both methods led to hydantoin attachment a significant difference was observed in the attachment of the PFOA group. The difference will be discussed later in section 6.3.

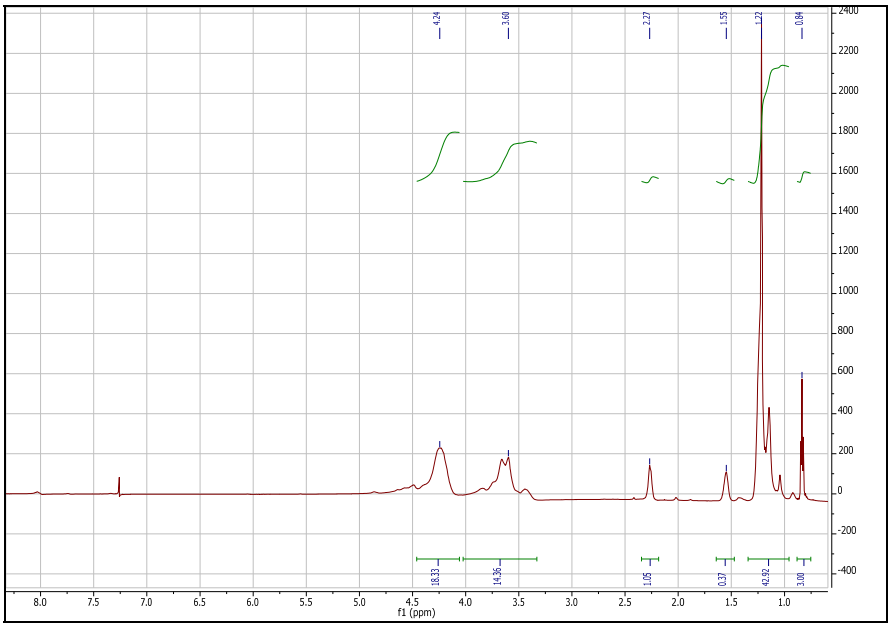


Figure 12. $^{1}$H NMR spectrum of intermediate 5.

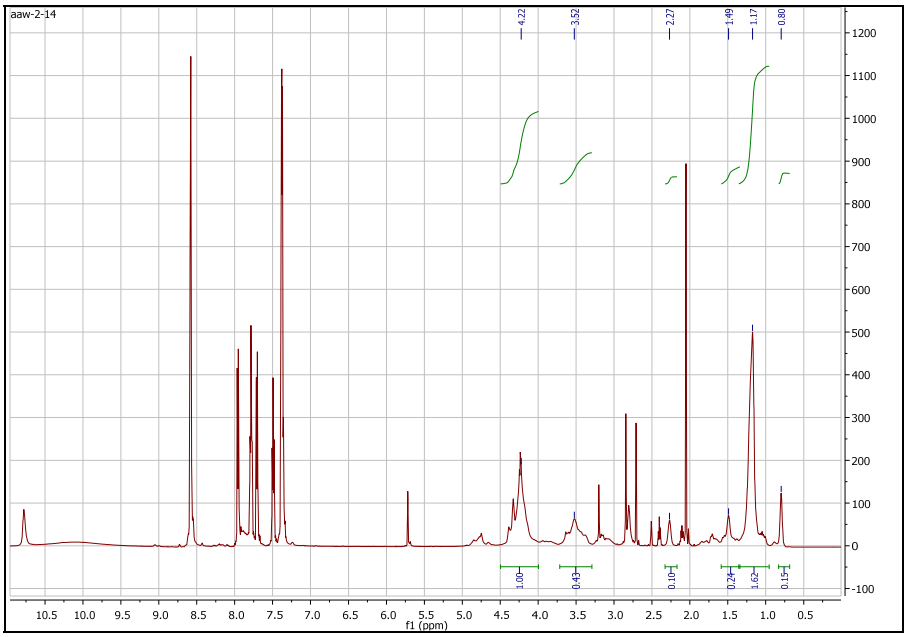


Figure 13. $^{1}$H NMR spectrum of DCC coupling of 5-hydantoin acetic acid and 4.

## 4. Target 2 Synthesis

Using microwave-driven reaction chemistry, target 2 was synthesized (figure 14) by attaching a hydantoin-silane (compound 6) to intermediate 5 that already contained perfluorinated and aliphatic groups. Reaction conditions were optimized by varying parameters, such as reaction time, power, and solvent. Microwave reactions were conducted in a CEM Corp Discover/Explorer Microwave Reactor NP-1008.

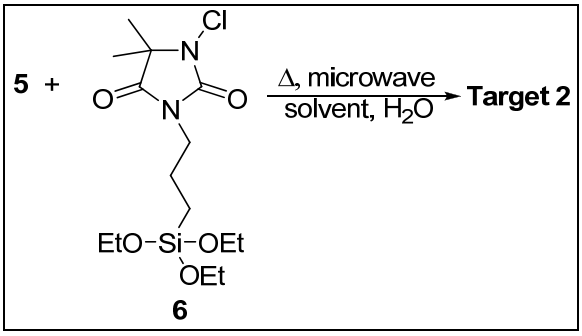


Figure 14. Microwave synthesis of target 2. Solvent = DMF, Toluene, THF, and DCM.

The initial sets of reactions used experimental conditions shown in table 1, and all reactions yielded gummy solids. $^{1}$H NMR characterization (discussed later) indicated the presence of a competing condensation reaction between siloxane groups that yielded a siloxane network instead of the desired product.

Table 1. Initial attachment of hydantoin-silane via microwave chemistry.

| Method | Experimental Conditions | | | | |
|---|---|---|---|---|---|
| | Power (W) | Reaction Interval (s) | Total Reaction Time (min) | Solvent | mmol of Hydantoin-Silane |
| Fixed Power | 150 | 30 and 60 | 4.5 | DMF | 3 |
| Fixed Power | 300 | 30 | 5 | Toluene | 1.7 |
| Power Cycling | 150 | 30 | 6 | THF | 1.7 |

To combat the condensation reaction, stoichiometric conditions were altered as shown in table 2. Low boiling solvents, such as DCM and THF, were used instead of the initial high-boiling solvents (e.g., toluene, DMF). To reduce the possibility of competing condensation reactions lower hydantoin-silane concentrations (0.2–0.4 mmol equivalents) were used instead of the initial excess (1.7–3 mmol equivalents).

Table 2. Optimized attachment of hydantoin-silane via microwave chemistry.

| Power Cycle | Experimental Conditions | | | | |
|---|---|---|---|---|---|
| | Power (W) | Reaction Interval (s) | Total Reaction Time (min) | Solvent | mmol of Hydantoin-Silane |
| 1 | 150 | 30 | 4.5 | THF | 0.2 |
| 2 | 150 | 30 | 4.5 | DCM | 0.2 |
| 3 | 150 | 30 | 4.5 | DCM | 0.4 |
| 4 | 150 | 60 | 9 | DCM | 0.4 |
| 5 | 300 | 30 | 4.5 | DCM | 0.4 |
| 6 | 300 | 60 | 9 | DCM | 0.4 |

Note: All experiments used the power cycling method.

## 4.1 Characterization of Target 2

Initial reaction conditions for the microwave synthesis of target 2 were unsuccessful. A typical $^{1}$H NMR spectrum of reaction products for this set of conditions (figure 15) showed a substantial hydantoin-silane signal, which overwhelmed the miniscule Boltorn polymer signals. The silane group of compound 6 underwent self-condensation reactions to form an undesired silane network, which is similar to a sol−gel formation.

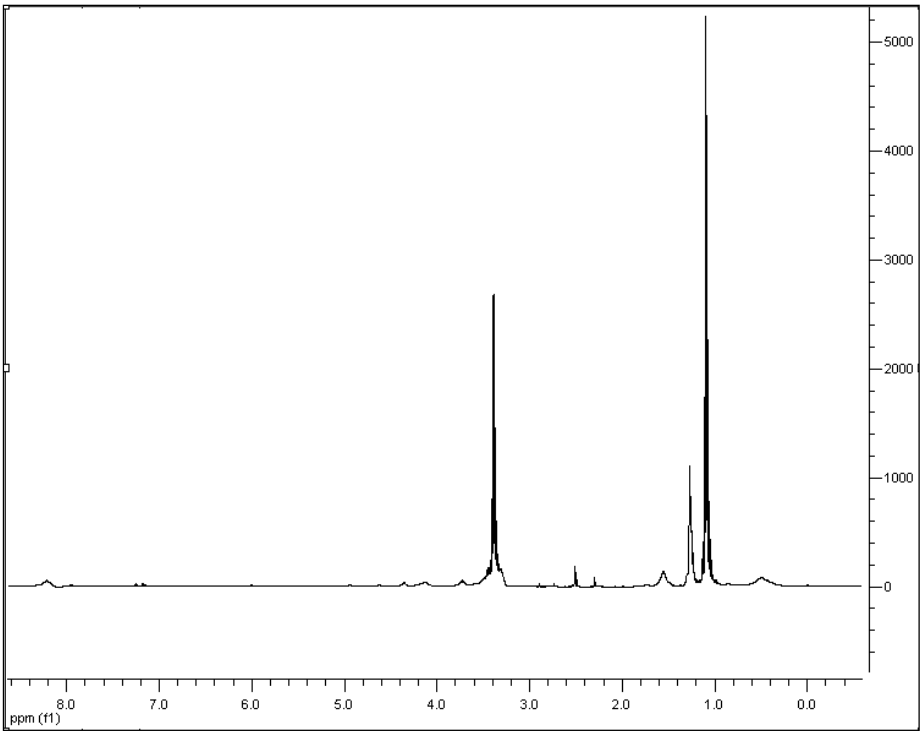


Figure 15. Representative $^{1}$H NMR spectrum of initial microwave experiments.

Once the reaction parameters were adjusted to those shown in table 2 reaction products changed from gummy solid to viscous liquids. The $^{1}$H NMR spectra (figure 16) for all the products analyzed indicate conversion of alcohol group into ester group with a resulting ester-alcohol ratio of 1:0.67. All spectra from this series looked very similar, so that only one representative plot is shown. The results indicated that solvent, power (W), and reaction time within tested parameters did not have a noticeable effect on product formation. However, decreasing the amount of compound 6 from an excess (table 1) to a lesser amount (0.2–0.4 mmol, table 2) was very beneficial. The change allowed an assessment of the extent of reaction, because the integrals of Boltorn polymer signals could be measured unlike reaction products obtained from reactions that used an excess amount of compound 6.

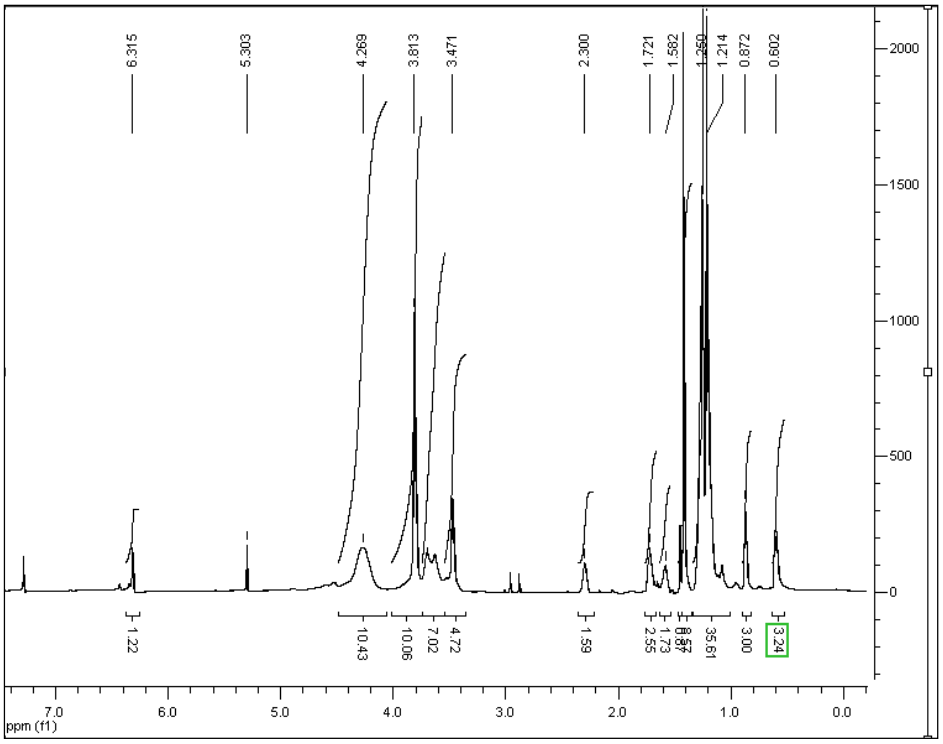


Figure 16. Representative $^{1}$H NMR of reaction product of follow-up microwave experiments listed in table 2.

## 5. Target 3 Synthesis

The nonchlorinated precursor to target 3, (intermediate 8), was obtained by adding the chloroacetyl moiety to intermediate 5 via acid halide chemistry and resulted in 83% yield of product. The successive step involved a $S_N2$ displacement, substituting the chloride group with the potassium salt of 5,5-dimethylhydantoin (figure 17). Optimization of reaction conditions (e.g., low temperatures and nitrogen atmosphere) led to the desired product in 65% yield.

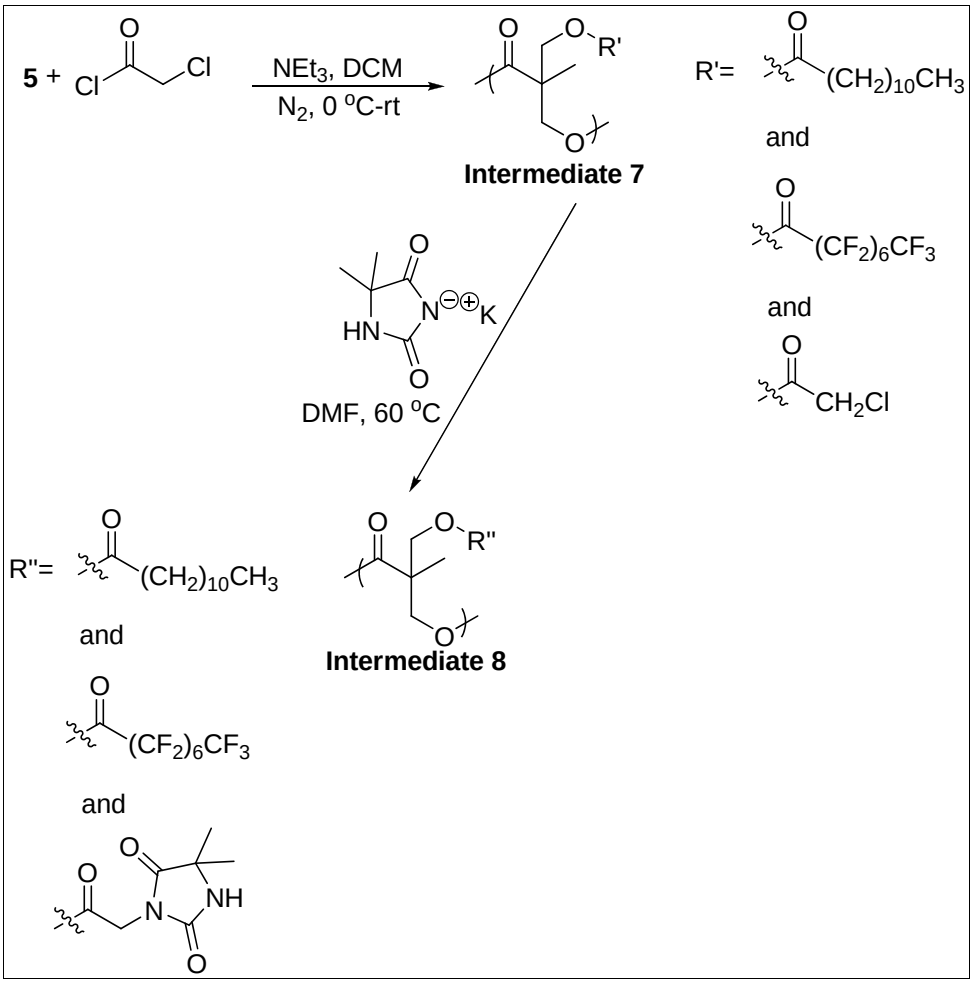


Figure 17. Attachment of the 5,5-dimethylhydantoin group to Boltorn H20 polymer.

## 5.1 Characterization of Target 3

The synthesis of target 3 was undertaken due to the propensity of the chlorinated 5-hydantoin acetic acid group to produce HCl through an elimination process, reducing its functionality by 50% (figure 18). To prevent the elimination 5,5-dimethylhydantoin was substituted for 5-hydantoin acetic acid, because it lacks the adjacent C−H proton to participate in the elimination to produce HCl.

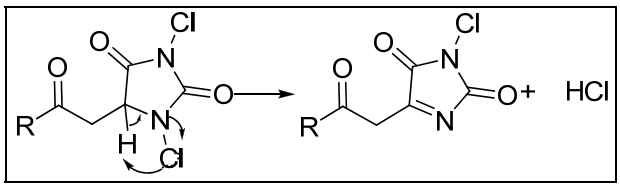


Figure 18. Production of HCl by chlorinated hydantoin moiety.

$^{13}C$ NMR and $^{1}H$ NMR analysis were used to evaluate the conversion of intermediate 5 into the chloromethylene-Boltorn polymer (intermediate 7) as shown in figure 17. Similar analysis was also used to evaluate attempts to attach the 5,5-dimethylhydantoin group to intermediate 7 via $S_N2$ chemistry.

Formation of intermediate 7 was verified by the presence of a methylene group (figure 19, peak C) that indicates successful addition of the chloroacetyl moiety. In the subsequent $S_N2$ reaction, the chloromethylene peak was consumed. The disappearance of the chloromethylene peak (figure 20), coupled with the appearance of the hydantoin methyl group (figure 20, peak D) confirm the formation of 8. The proton of the N−H bond was not resolvable for direct observation. The $^{13}C$ NMR spectrum of intermediate products 7 (figure 21) and 8 (figure 22) also supported product formation. Specifically, peaks A and B (176.95 ppm and 155.29 ppm, respectively) in figure 22 corresponded to the carbonyl groups of the hydantoin group. Those peaks are not observed in figure 21, and, therefore, corresponding groups are not present in intermediate 7.

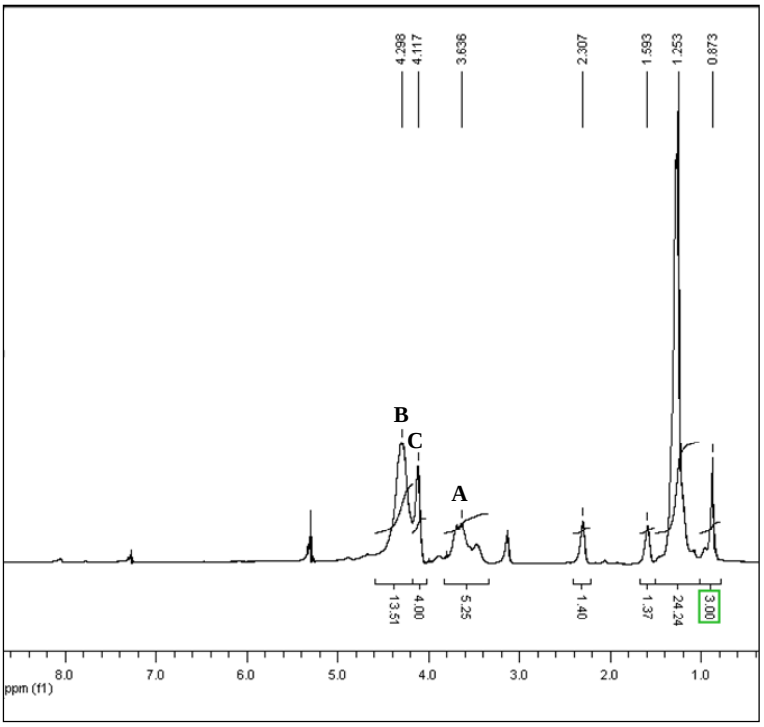


Figure 19. $^{1}H$ NMR spectrum of 7.

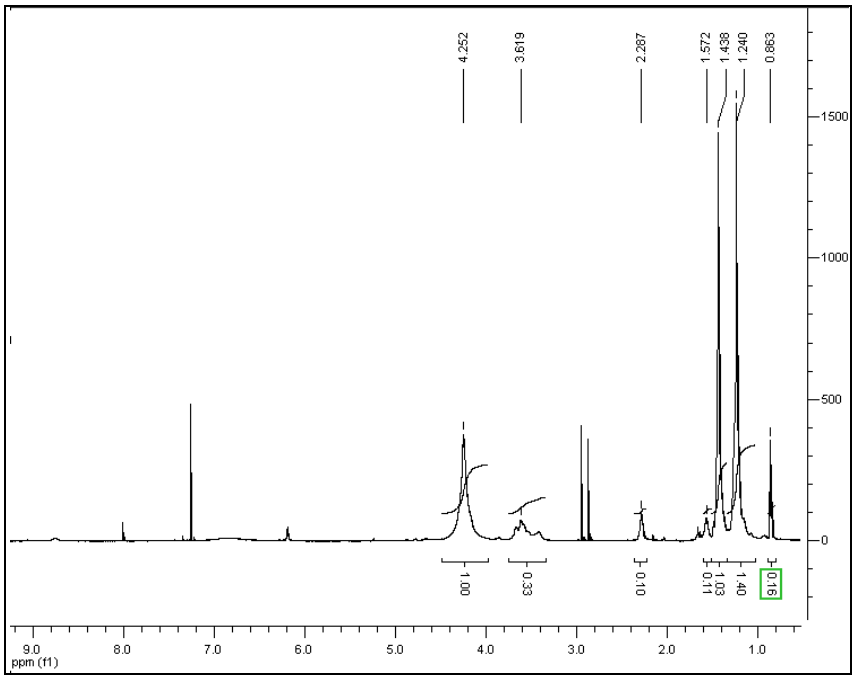


Figure 20. $^{1}$H NMR spectrum of intermediate 8.

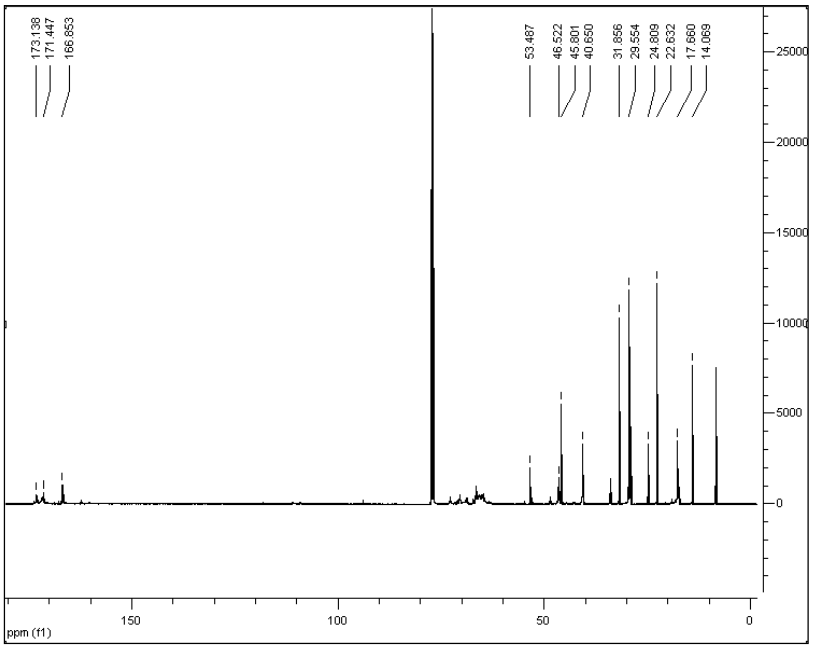


Figure 21. $^{13}$C NMR spectrum of intermediate 7.

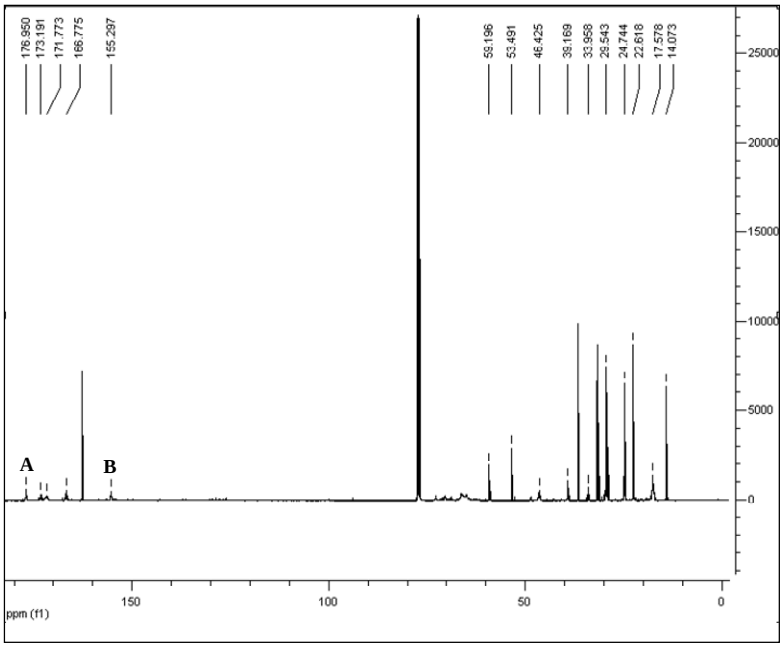


Figure 22. $^{13}C$ NMR spectrum of intermediate 8.

# 6. Chlorination and X-Ray Photoelectron Spectroscopy

## 6.1 Model Film Formulation and Deposition

Intermediates 4 and 5 were formulated for use as films using Estane 58237 (a thermoplastic polyurethane, TPU) as the primary polymer matrix. Both the TPU and intermediates were dissolved in THF; the solutions were then combined to afford formulations containing 2% additive (intermediates 4 or 5) relative to the total solids of the solutions. The solutions were cast onto glass cover slips and allowed to dry in a desiccator overnight at ambient temperature and then dried an additional 18 h at 50 °C. The anticipated behavior of the additives is that the PFOA groups would drive the spontaneous enrichment of the intermediates at or near the air-polymer surface of the TPU film. The proximity of the attached hydantoin moiety would then allow its interaction with chemical agents or bleach (to regenerate the N−Cl functionality).

## 6.2 Chlorination of Model Films

Following preparation, the films were treated with 13% aqueous bleach to determine the viability of (re)charging surfaces with the oxidizing functionality (N−Cl). The bleach treatment should transform intermediate 4 into target 1 by converting the NH group of the hydantoin moiety into an N−Cl group, yielding the stabilized $Cl^+$. Films infused with intermediate 5 should not contain chlorine, because they do not contain the hydantoin group. Their inclusion was to verify that bleach treatment would not alter the core polymer by chlorination of the amide NH group of the TPU matrix.

Three different chlorination methods were evaluated in an attempt to chlorinate the hydantoin group. In the first approach, referred to as the Dipping Method, the polymer films on the glass substrate were immersed 10 times into bleach for 1 s intervals and then air dried. In the second method, designated the Soaking Method, each film was soaked in bleach for 2 min, shaken free of excess bleach, and allowed to air dry. In the third method, films were inverted over a container filled with bleach, at a distance of ~10 mm, and the films were exposed to the vapor of the bleach solution for ca. 18 h (Vapor Method).

### 6.3 Characterization of Surface Properties

XPS was performed on a Kratos Axis Ultra photoelectron spectrometer using an Al monochromatic x-ray source at 100 W with base pressure $1.0 \times 10^{-8}$ Torr. XPS measures x-ray generated photoelectrons, providing elemental and chemical oxidation state information. The measured photoelectrons escape from the top 10–12 nm of the film, limiting the depth of observation for XPS measurements. All elements except H and He can be detected. The quantitative results provided below are expressed in terms of atomic percent concentration. Care should be taken when comparing atomic percent to the more commonly considered weight and mole percent. Atomic percentages from XPS neglect hydrogen in the sample, so that this caveat must be considered as the data is reviewed. Complete results of atomic composition on the surface of the analyzed materials are shown in table 3.

Table 3. Atomic concentration percent at film surface.

| Films | Atomic Concentration | | | | |
|---|---|---|---|---|---|
| | Cl | F | C | N | O |
| **Nonchlorinated Controls** | | | | | |
| Estane Control | 0.00 | 0.00 | 84.6 | 1.81 | 13.6 |
| Intermediate 4 | 0.00 | 0.00 | 79.6 | 3.24 | 17.2 |
| Intermediate 5 | 0.00 | 11.2 | 66.9 | 1.91 | 20.0 |
| **Dipping Method** | | | | | |
| Estane Control | 0.42 | 0.00 | 82.3 | 2.08 | 17.1 |
| Intermediate 4 | <0.1 | 0.00 | 80.8 | 2.16 | 17.1 |
| Intermediate 5 | 0.33 | 11.4 | 68.5 | 2.01 | 17.8 |
| **Soaking Method** | | | | | |
| Estane Control | 1.81 | 0.00 | 82.3 | 1.41 | 14.5 |
| Intermediate 4 | 0.63 | 0.00 | 79.7 | 2.51 | 17.1 |
| Intermediate 5 | 0.26 | 13.7 | 66.6 | 2.07 | 17.4 |
| **Vapor Method** | | | | | |
| Intermediate 4 | 0.00 | 0.00 | 76.1 | 3.68 | 20.2 |
| Intermediate 5 | 0.00 | 15.6 | 64.5 | 1.05 | 19.0 |

Note: The percentages for other elements, such as Na, K, Si, and Ti were not reported.

None of the chlorination methods produced a substantial level of chlorine on film surfaces. The Vapor Method did not produce chlorine on any surface. The lack of fluorine in intermediate 4 samples was important, because it indicated that DCC coupling reactions did not attach the PFOA. The melt condensation product contained substantially more fluorine than the product

obtained via DCC coupling. The lack of fluorine probably led to a decrease or failure of the additive to migrate effectively to the surface of the films. The Soaking Method led to more chlorine content than the Dipping Method, suggesting that the increased chlorine content could be due to the longer contact time of the coating with bleach using the Soaking Method versus the Dipping Method. Intermediate 5 samples did contain a small amount of chlorine, which was unexpected, because these samples lacked the hydantoin group. The chlorine content likely resulted from incomplete washing after the bleach exposure, or it may reflect the baseline chlorine retention of the TPU (retaining chloride via the aliphatic amide bond in the urethane backbone) (*1–10*). Control samples, which contained no polymer additives, were treated to the Soaking and Dipping Methods. These samples were shown to contain low levels of chlorine, which suggested that the levels of chlorine detected in the intermediates 4 and 5 samples were due to chlorine retention by the TPU. Because of the lack of fluorine in intermediate 4 it cannot be concluded that the chlorination with bleach was unsuccessful, because the hydantoin group was not present at the surface. This could indicate that the molecule of interest was buried in the bulk of the Estane film and was inaccessible for the XPS analysis.

We have previously shown good retention of Boltorn-based hyper branched polymers in polymer matrices, but those were functionalized using relatively hydrophobic pyrene butyrate ester chain ends (*12*). The hydantoin moiety is significantly more polar than the pyrene chain ends and may increase the susceptibility of the additive to be removed from a swellable matrix by successive washes.

## 7. Conclusions

Synthesis of the polymer target 1 was completed successfully; however, the chlorination of films incorporating this additive was largely unsuccessful. Because of concerns regarding instability of the N−Cl bond, and the possibility of an elimination product producing HCl, a decision was made that this reaction path would not serve the current goals of the project and was suspended. Expertise obtained during the synthetic experiments did, however, result in development of a synthetic scheme that led to the successful attachment of 5-hydantoin acetic acid to the hyperbranched polyester scaffold and have provided a number of viable protocols for the formation of activated ester bonds as a route to hyperbranched polyester modification.

The synthesis and characterization of the polymer target 2 were indicative of the desired product formation, however, further work is required in the optimization and characterization of the reaction and its products. A nonchlorinated precursor to target 3 was successfully synthesized, but attempts to chlorinate the hydantoin moiety were unsuccessful. Ongoing research to use the hydantoin moiety on a hyperbranched polymer scaffold has concluded.

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## List of Symbols, Abbreviations, and Acronyms

| | |
|---|---|
| $^{13}C$ NMR | carbon 13 NMR |
| $^{1}H$ NMR | proton NMR |
| AFRL | Air Force Research Laboratory |
| ARL | Army Research Laboratory |
| CARC | chemical agent resistant coating |
| $CDCl_3$ | chloroform |
| $Cl^+$ | oxidative chlorine |
| CWA | chemical warfare agent |
| d | day |
| DCC | dicyclohexylcarbodiimide |
| DCM | dichloromethane |
| DIC | diisopropylcarbodiimide |
| DMAP | *N*,*N*-dimethylaminopyridine |
| DMF | *N*,*N*-dimethylformamide |
| DMSO | dimethylsulfoxide |
| DPTS | 4-(dimethylamino)pyridinium 4-toluenesolfonate |
| DOD | Department of Defense |
| g | gram |
| HD | bis(2-chloroethyl) sulfide |
| HOBT | *N*-Hydroxybenzotriazole |
| mol | mole |
| $N_2$ | nitrogen |
| NMP | 1-methyl-2-pyrrolidinone |
| NMR | nuclear magnetic resonance |

| | |
|---|---|
| NRL | Naval Research Laboratory |
| PFOA | perfluorinated octanoic acid |
| rt | room temperature |
| $S_N2$ | bimolecular nucleophilic substitution |
| THF | tetrahydrofuran |
| VX | O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate |
| XPS | x-ray photoelectron spectroscopy |

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